51

THE DIELECTRIC PROPERTIES OF COPAL ESTER

A. K. SEN and G. N. BHATTACHARYA

DEPARTMENT OF APPLIED PHYSICS, CALCUTTA UNIVERSITY

(*Received, July* 27, 1960)

ABSTRACT. The dielectric properties of copal ester have been measured over a wide range of temperature and frequency viz., from 25°C to 160°C and from 400 c/s to 300 kc/s. Within the temperature range of investigation copal ester behaves as a typical polar resin in the anomalous dispersion range. The loss curves have unusually broad peaks which suggest a highly distributed relaxation time of its orientating polar units. This is corroborated from the shape of the $\varepsilon''/\varepsilon_m''$ *vs* log f/f_m curve as well as a high value of the distribution factor calculated from the Cole and Cole diagram. With the help of melt viscosity data of this resin the size of its rotating unit has been calculated following Debye's relation and the calculated radius comes out to be about 1.5 Å, which is the same as that of a hydroxyl group. The presence of the hydroxyl group is clearly indicated in the infrared absorption spectrum of this resin, which suggests these groups to be its actual rotating units.

INTRODUCTION

Copals are a general name for various fossil and semi-fossil resins found in some tropical countries. They are usually named after their places of origin. Like rosin, copals have a high acid value and they differ somewhat in their chemical and physical properties depending upon their composition. Copal esters, however, are important as they are widely used in the preparation of insulating varnishes, impregnating compounds, moulded insulation etc.

Bhattacharya (1946) studied the dielectric properties of Manila Copal, while Clare (1949) reported the dielectric properties of Kauri copal. But recently the application of Debye's equation for obtaining the size of the rotating unit in a few natural resins has revealed some interesting fact. In the case of rosin (Sen and Bhattacharya, 1958a) the radius obtained is equal to the effective radius of abietic acid molecule, the chief constituent of rosin, whereas in the case of ester gum (Sen and Bhattacharya, 1958b) which has a much bigger molecule, a similar calculation yields a much smaller value for the radius, viz., that of the hydroxyl group. The fact that ester gum contains hydroxyl group has been corroborated later from the infrared absorption curve.

It was concluded, therefore, that perhaps the unesterified hydroxyl groups of mono- and di-abietates in ester gum were the actual rotating units. If now mono- and di-abietates are formed during the esterification of rosin, it is natural to expect

a similar formation of mono- and di-glycerides during the esterification of similar other resins with glycerol. If in these esters too the value of the radius comes out to be that of the hydroxyl group our conclusions regarding the rotating unit in ester gum can be justified to some extent. With this end in view the measurement of the dielectric properties of the glycerol esters of copal has been undertaken.

THEORETICAL AND EXPERIMENTAL

The theoretical aspects of dielectric measurement have been fully discussed before (Sen and Bhattacharya, 1958a and 1958b) and the procedure for the measurement of permittivity, power factor, resistivity and viscosity are the same as reported earlier (Sen and Bhattacharya, 1957, 1958*a* & b).

Infrared absorption curves

(1) *Recording of absorption curves*

Absorption measurements were done on a Hilger infrared spectrophotometer, model H 800, using a rock-salt prism as the dispersion element in the range of 1 to 15 microns. The instrument was used in the double beam position, where the transmission through the test medium was automatically balanced with the transmission through air. A Brown-Electronik recording potentiometer was used for obtaining the absorption-wavelength curve. This curve was photographically reduced to convenient size.

(2) *Preparation of test-pieces.*

Wires of 28 S.W.G. were made into rectangular frames of dimensions approximately $1'' \times \frac{1}{2}''$. Films were formed on the wire frames from molten resin having appropriate viscosity and surface tension depending upon temperature. Sufficient care was taken in preparing the films of required thickness making a compromise between maximum transmission and mechanical stability.

DISCUSSION

The results of measurement of dielectric constant ϵ', dielectric loss ϵ'', and power factor $\tan \delta$ for various temperatures and frequencies are shown graphically in Figs. 1, 2, and 3 respectively.

These curves also indicate the characteristics of a typical polar substance in the anomalous dispersion range. The power factor as well as the dielectric loss curves begin to rise from about 50°C. The loss maxima for 10 kc/s, 50 kc/s, 100 kc/s and 300 kc/s are more or less of the same value and it is about 0.09 while for 400 c/s and 1 kc/s they are slightly higher. The range of temperature over which the different peaks are distributed is about 42°C.

The striking feature of these loss curves is their unusually broad peaks. The dielectric constant curves are also flat. The nature of these curves indicates

the effects of distributed relaxation time in a greater degree. From Fig. 4 it may also be seen that the region of dispersion spreads over at least 5 to 6 decades

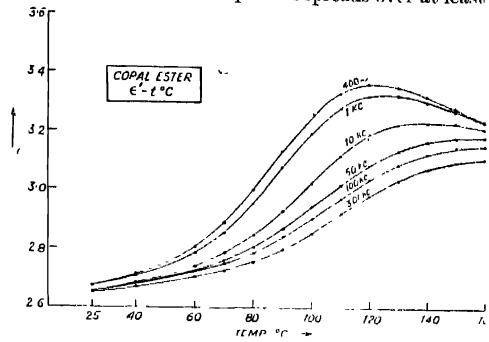

Fig. 1

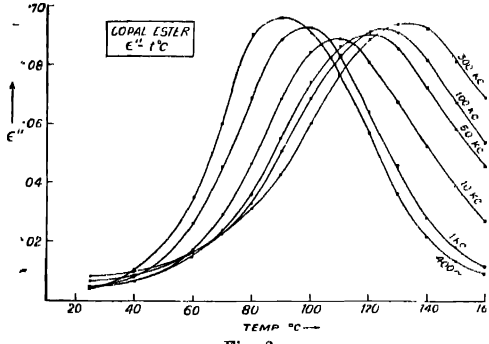

Fig. 2.

of frequency. The Cole and Cole diagram for this resin is shown in Fig. 6. Although the experimental curve is a circular arc its centre lies considerably below the abscissa signifying a wide distribution of relaxation times. The value of the distribution factor h calculated from the diagram is 0.69 compared to 0.52 for ester gum. The ϵ''/ϵ''_m vs $\log f/f_m$ curve in Fig. 7 also reveals this high degree of distribution.

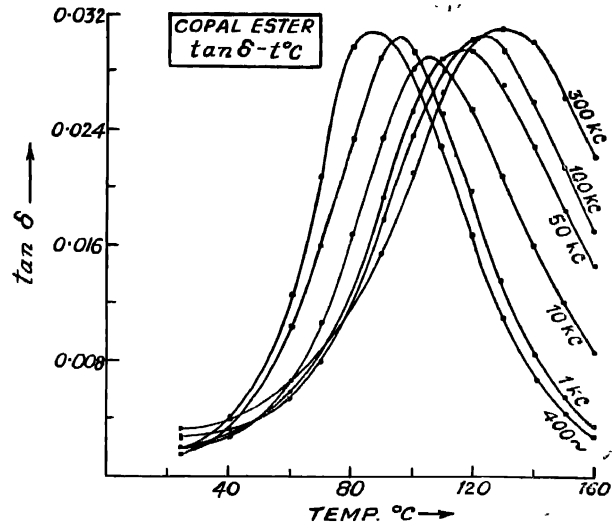
COPAL ESTER
tan δ-t°C
0·032
0·024
0·016
0·008
tan δ
300 KC
100 KC
50 KC
10 KC
1 KC
400 ~
40
80
120
160
TEMP. °C

Fig. 3.

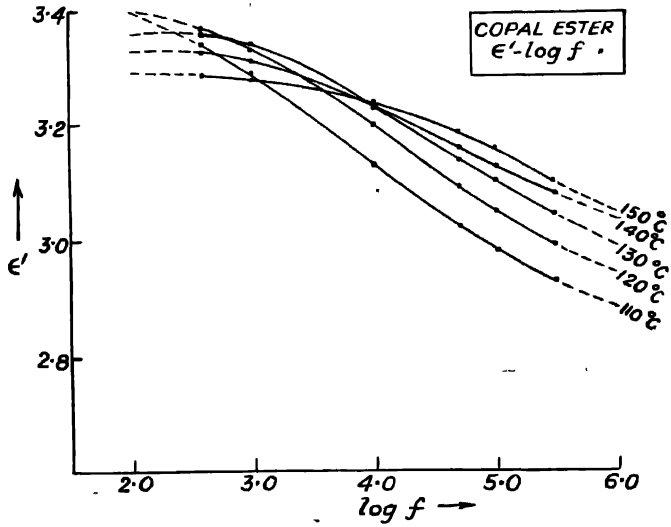
COPAL ESTER
ε'-log f
3·4
3·2
3·0
2·8
ε'
150 °C
140 °C
130 °C
120 °C
110 °C
2·0
3·0
4·0
5·0
6·0
log f

Fig. 4.

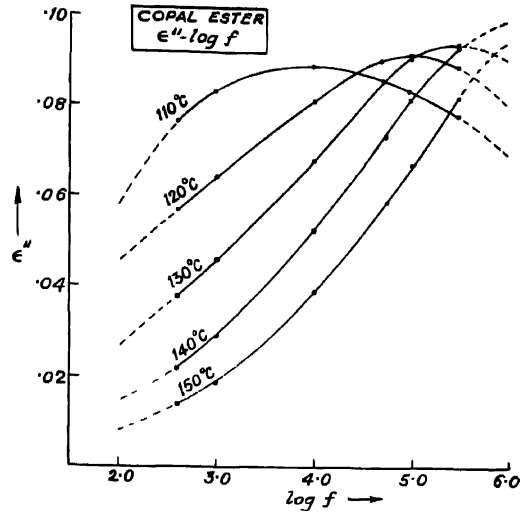
COPAL ESTER
ε''-log f
·10
·08
·06
·04
·02
ε''
110°C
120°C
130°C
140°C
150°C
2·0
3·0
4·0
5·0
6·0
log f

Fig. 5.

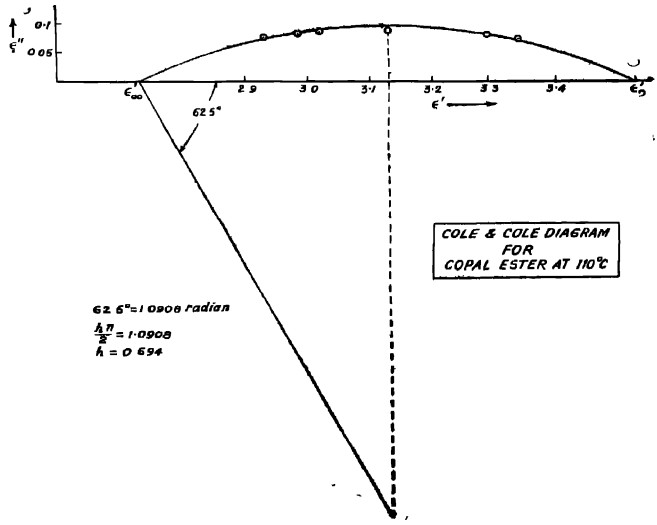
0·1
ε'' 0·05
ε∞'
2·9
3·0
3·1
3·2
3·3
3·4
ε₀'
ε'
62·5°
COLE & COLE DIAGRAM
FOR
COPAL ESTER AT 110°C
62·5°=1·0908 radian
h π/2 = 1·0908
h = 0·694

Fig. 6.

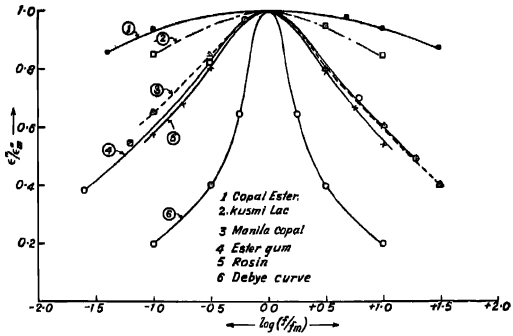

Fig. 7.

We may now calculate the value of the radius of the rotating unit in this resin from the relaxation time at the temperature of a loss-maximum and its melt viscosity at that temperature

The melt viscosity of copal ester was determined in the same way as in the case of other resins. The results are shown in Table 1 and the graph of log η against $1/T$ is shown in Fig. 8.

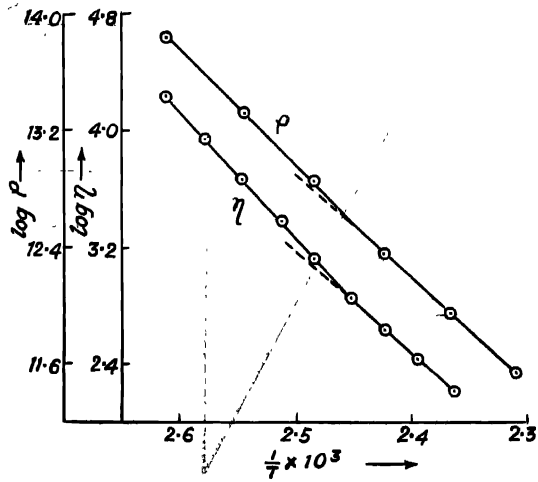

Fig. 8.

TABLE I

Viscosity—temperature data

Temperature		$\frac{1}{T} \times 10^3$	Viscosity η in poise	log η
t°C	T°K			
110	383	2 611	16,630	4.2208
115	388	2.577	8,710	3.9400
120	393	2.545	4,480	3.6513
125	398	2 513	2,400	3 3802
130	403	2 481	1,320	3 1205
135	408	2.451	680	2 8325
140	413	2.421	420	2 6232
145	418	2 392	260	2 4150
150	423	2 364	160	2.2041

For comparing the internal friction involved in viscosity and resistivity, the curve of log ρ plotted against $1/T$ is incorporated in the same figure. Resistivity and conductivity data are given in Table II.

TABLE II

D.C. conductivity or resistivity—temperature data

Temperature		$\frac{1}{T} \times 10^3$	Conductivity k in mho cm^{-1}	Resistivity ρ in ohm cm	log ρ
t°C	T°K				
110	383	2.611	0.152×10^{-13}	$6\ 575 \times 10^{13}$	13.8179
120	393	2.545	0.475×10^{-13}	$2\ 104 \times 10^{13}$	13 3231
130	403	2 481	0.146×10^{-12}	6.837×10^{12}	12 8349
140	413	2 421	0.437×10^{-12}	$2\ 289 \times 10^{12}$	12.3595
150	423	2.364	0.112×10^{-11}	8.940×10^{11}	11.9513
160	433	2 309	0.284×10^{-11}	3.525×10^{11}	11.5471

The slopes of both the viscosity and resistivity curves are identical signifying that the same energy of activation is involved in both the processes. As in the case of oster gum (Sen and Bhattacharya, 1957) a transition point is also seen in this resin near about 130°C. The slopes of both the viscosity and resistivity curves change abruptly at this temperature in a similar way signifying some change of state at this temperatue,

The radius of the rotating unit is computed using Debye's equations and the results are shown in Table III.

TABLE III

Calculated relaxation time and radius of the rotator

Frequency in kc/s	Loss maximum temperature t_m in °C	Relaxation time τ in sec.	log η at t_m	Radius of the rotator a in Å
10	110	1.424×10^{-5}	4.22	1.53
50	121	2.859×10^{-6}	3.00	1.45
100	127	1.434×10^{-6}	3.26	1 50
300	135	$4\ 808 \times 10^{-7}$	2 82	1 48

The chemical composition of manila copal has been studied by various workers and according to them it consists of several acids. According to Tschirch and Koch (1902) the major constituents of manila copal (comprising about 75% of the total) are two isomeric forms of mancopalic acid, viz., α and β-mancopalic acid having the chemical formula $C_{19}H_{17}COOH$. Other constituent acids have more or less similar chemical formula. Therefore, glycerol esters of these acids should—even on a moderate estimate, be big molecules—much bigger than the values shown in Table III. Therefore, rotation of the entire molecule seems improbable in this resin also. A segment or a part of the molecule or some groups attached to it may be the actual rotator here.

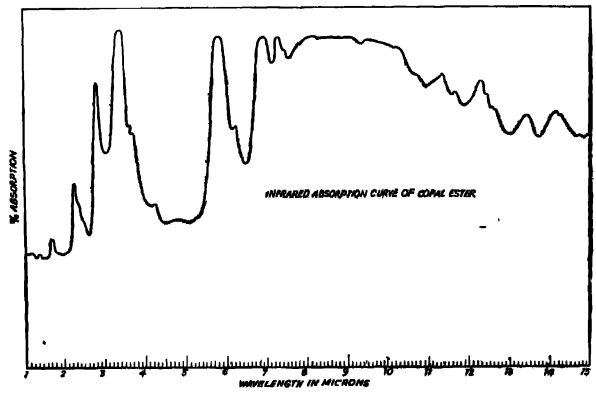

Fig. 9.

The values of the radii obtained are the same as in the case of ester gum, viz., that of a hydroxyl group. The presence of hydroxyl groups in ester gum has been conclusively proved and they can be explained as due to the presence of mono- and di-glycerides formed during the esterification of rosin with glycerol. In copal ester also the presence of hydroxyl groups can be similarly expected. But this view can be justified if their presence can be similarly demonstrated on the basis of other evidences.

From the infrared absorption curve shown in Fig. 9 it may be seen that an absorption peak occurs at the wavelength of 2.78μ signifying the presence of hydroxyl groups also in this resin as in the case of ester gum.

ACKNOWLEDGMENTS

The authors are grateful to the Director, Central Glass and Ceramics Research Institute, Calcutta, under the Council of Scientific and Industrial Research Government of India, for providing them with the facilities available there for obtaining the infrared absorption spectrogram of this resin They also wish to express their thanks to Messrs. Jenson and Nicholson (India) Ltd. for the supply of a sample of copal ester.

REFERENCES

Bhattacharya, G. N., 1946, *J. Sc. & Ind. Res*, **4B**, 713.

Claro I. C., 1949, Elastomers and Plastomers (Elsevier Publishing Co., New York), **2**, 371.

Sen, A. K and Bhattacharya, G. N., 1957, *J. Assoc. App. Physicists.*, **4**, 72.

Sen A K. and Bhattacharya G. N., 1958a, *Ind. J. Phys.*, **32**, 556.

Sen A. K. and Bhattacharya, G. N., 1958b, *Ind. J. Phys.*, **32**, 49

Tschirch and Koch, 1902, *Arch. Pharm.*, **240**, 202.